AD-A159 623 ROTATING DISC VOLTAMMETRY AT POLYPYRROLE MODIFIED ELECTRODES(U) CINCINNATI UNIV OH DEPT OF CHEMISTRY OCT 84 N00014-84-C-2194 1/1

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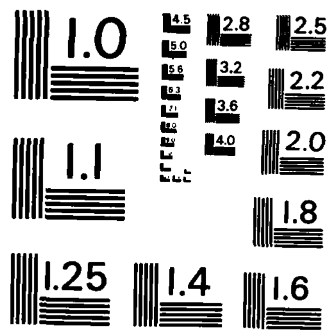

MICROCOPY RESOLUTION TEST CHART
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University of Cincinnati, Department of Chemistry, Cincinnati, OH 45221

Title: Rotating Disc Voltammetry at Polypyrrole Modified Electrodes
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FINAL REPORT: ONR CONTRACT N00014-84-C-2194

The nature and uniformity of insitu electrogenerated Polypyrrole Films (PPF's) are strongly influenced by the nature of the electrode, deposition potential and uniformity of the current density at the electrode surface. A uniform current density during deposition is absolutely essential. In general, it appears that deposition first occurs at isolated active sites followed by radial growth out from these sites. This phenomonae appears to occur at all materials studied but seems more pronounced on SnO_2 coated glass than on metal surfaces. The optimal electropolymerization potential found in this study (+1000 mV) is well into the oxidation wave of pyrrole. Other workers have found that the more uniform morphologies are obtained at +750 mV. However, there seems to be general agreement that the success rate for "good" films is worse at lower potentials. In our experience the use of potential pulses rather than a steady DC potential does not seem to improve PPF homogeneity, in contrast to the results obtained by other workers. In the early work on the synthesis of PPF's it was observed that the mechanical properties and the adherence of the films were improved by the addition of H_2O. Our results show that the addition of H_2O (1% or 2%) to the CH_3CN media leads to more irreproducibility in the uniformity of these films.

One important question about PPF electrodes relates the the mechanism of the transport of species to the electrochemically active surface. An interesting possibility is that an ionic gating mechanism is envolved and that electrochemically neutral PPF act as a relatively impermiable membrane and the oxidized PPF would be a porous membrane, with the electronically conducting polymer chains increasing the area of the electrode. This possibility was investigated using Rotating Ring Disk (RRD) techniques. Assuming the hypothesis were true, the limiting currents for benzoquinone oxidation would decrease, due to the neutral PPF impeding its transport to the electrode surface while the limiting currents for the oxidation of Ferrocene should increase, due to the increase of the electrode area. However, the limiting currents obtained, using ferrocene and benzoquinone solutions, showed no differences between PPF modified platinum and that of the bare platinum electrodes. This leads to the conclusion that PPF act as a very porous membrane on platinum electrodes in both the oxidized, conducting state and the neutral, non-conducting form. This conclusion is supported by the fact that Cyclic Voltammetry at the PPF modified and the platinum electrode in mixed Fc/BQ solution showed no difference for either couple. Further, the Fc/BQ results show the neutral PPF grown are porous enough to allow the BQ to diffuse to the electrode surface. Diaz et al. showed contradictory results for a similar experiment with nitrobenzene/ferrocene mixed solution, observing that the nitrobenzene peak reduces significantly in the same type of switching experiment (the couple were Fc/nitrobenzene). Since their film were electropolymerized at +800 mV, the difference may well mean that the density of the films grown by Diaz was greater. The argument that the electron transfer of ferrocene occurs at the PP/CH_3CN interface is not completely eliminated by these results. However, this conclusion is inconsistent with two facts: the porosity of PPF has been shown to be greater in the conducting form and the benzoquinone limiting currents are the same as those observed at the bare platinum electrode.

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